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**MODIFICATION OF BISPHENOL-A
BASED BISMALIMIDE RESIN (BPA-
BMI) WITH AN ALLYL-TERMINATED
HYPERBRANCHED POLYIMIDE (AT-
PAEKI)**



Haihu Qin, Patrick T. Mather, Jong-Beom Baek, and Loon-Seng Tan

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14. ABSTRACT As a continuation of previous work involving synthesis of an allyl-functionalized hyperbranched polyimide, AT-PAEKI, we have studied the use of this reactive polymer as a modifier of bisphenol-A based bismaleimide resin (BPA-BMI). This was pursued in anticipation of improvements in processability as well as physical properties including glass transition temperature, elastic modulus, and fracture toughness. Apparent miscibility, indicated by optical clarity with a single T _g , was observed for compositions containing up to 16 wt% AT-PAEKI. Additionally, we observed complete suppression of monomer crystallization and a slight increase in the overall cure exotherm. By rheological characterization, blends containing 4 wt% AT-PAEKI were found to feature a dramatic (65-fold) reduction in the viscosity minimum during heating. Dynamic mechanical analysis (DMA) showed that the addition of 2, 4, 8 wt% AT-PAEKI increases the cured modulus by approximately 10% from a base value of 3.4 GPa, while adding 16 wt% AT-PAEKI decreases the modulus slightly to 3.3 GPa. DMA also revealed that the cured glass transition temperature increases monotonically with the addition of AT-PAEKI. Our results showed a modest toughening effect upon the addition of AT-PAEKI. We conclude that AT-PAEKI may serve as an effective reactive processing aid with slight improvements in T _g , modulus, and fracture toughness.						
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Modification of bisphenol-A based bismaleimide resin (BPA-BMI) with an allyl-terminated hyperbranched polyimide (AT-PAEKI)

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Abstract

As a continuation of previous work involving synthesis of an allyl-functionalized hyperbranched polyimide, AT-PAEKI, we have studied the use of this reactive polymer as a modifier of bisphenol-A based bismaleimide resin (BPA-BMI). This was pursued in anticipation of improvements in processability as well as physical properties including glass transition temperature, elastic modulus, and fracture toughness. Apparent miscibility, indicated by optical clarity with a single T_g , was observed for compositions containing up to 16 wt% AT-PAEKI. Additionally, we observed complete suppression of monomer crystallization and a slight increase in the overall cure exotherm. By rheological characterization, blends containing 4 wt% AT-PAEKI were found to feature a dramatic (65-fold) reduction in the viscosity minimum during heating. Dynamic mechanical analysis (DMA) showed that the addition of 2, 4, 8 wt% AT-PAEKI increases the cured modulus by approximately 10% from a base value of 3.4 GPa, while adding 16 wt% AT-PAEKI decreases the modulus slightly to 3.3 GPa. DMA also revealed that the cured glass transition temperature increases monotonically with the addition of AT-PAEKI. Fracture toughness was gauged using the single edge notched beam methodology to yield the critical stress intensity factor, K_{IC} . Our results showed a modest toughening effect (from 0.48 to 0.55 MPa m^{1/2}) upon the addition of AT-PAEKI. We conclude that AT-PAEKI may serve as an effective reactive processing aid with slight improvements in T_g , modulus, and fracture toughness.

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1. Introduction

High performance thermosets (HPTs), such as epoxy and bismaleimide (BMI), are of great interest as the matrix resins for use in structural composites. Many of their favorable properties, including high glass-transition temperature and high modulus, are directly related to the underlying microstructure of high crosslinking density and rigid molecular network. However, this structural feature also results in an inherent brittleness of the material. In the past two decades, difference approaches to toughening HPTs have been investigated [1]. For example, one well-studied approach to

toughening epoxy is to add an elastomeric polymer as a modifier. Although this approach does improve the fracture toughness, it also brings about significant decreases in many desirable properties such as modulus and yield strength [2]. Another approach employs the high performance thermoplastic, for example, polyimides, as the toughening agents. Since this approach avoids incorporation of low T_g and low modulus species, it can yield increased fracture toughness with little compromise in T_g and modulus. However, a drawback is that this approach hampers processability: even at low molecular weight, such high performance plastic modifiers can increase the viscosity dramatically and make the material largely unprocessable [3].

Hyperbranched polymers (HBPs) offer a promising alternative for the toughening of HPTs. Because of their highly branched macromolecular architecture, hyperbranched polymers have many distinct properties when compared to conventional linear analogs. First of all, because of their compact spherical conformation, hyperbranched polymers

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usually have a Mark-Houwink exponent for dilute solution viscometry, α , less than or equal to 0.5. An example was given in the work by Möck et al. [4]. For their hyperbranched aromatic polyester, they found that the value of α decreased with increasing degree of branching (DOB). For a hyperbranched polymer with a DOB of 0.64, a value of 0.18 was found, in sharp comparison of 0.55 in the linear polymer control.

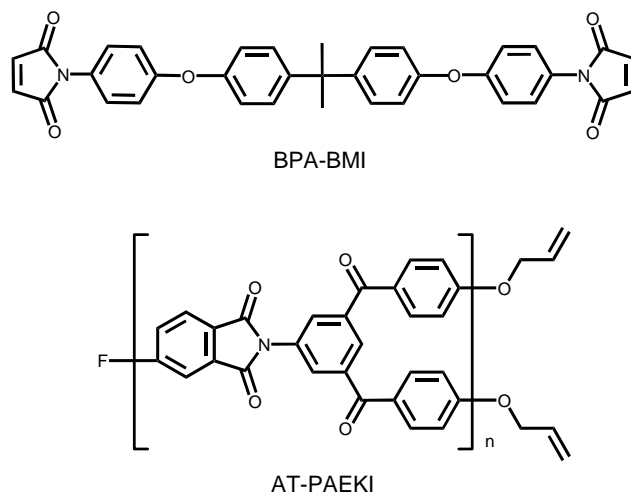
The spherical conformation also reduces the entanglements between the molecular chains, making the rheology of a HBP quite different from the conventional linear polymers. Two of the most distinct rheological properties associated with the HBPs are their Newtonian-like behavior and low viscosity. Hsieh et al. [5] studied the melt rheology of a series of commercial aliphatic hyperbranched polyesters, namely, Boltorn H[®] H20-H50. For those with low molecular weight and low generation number, a typical shear thinning behavior was found. On the other hand, for those with higher molecular weight and higher generation number, a Newtonian-fluid-like behavior was found. More interestingly, at the shear rate (frequency) of 10 s^{-1} , the low molecular weight HBPs had higher flow activation energy (around 140 kJ/mol) than higher molecular weight HBPs (around 100 kJ/mol). A similar observation was made when Magnusson et al. [6] studied the influence of DOB on the rheology of hyperbranched aliphatic polyesters: they found that the melt viscosity (dynamic, 6.28 rad/s) decreased as DOB increased. In addition, in the case of low DOB, a rubbery plateau was obvious, characteristic of the entanglement between the polymer chains. At high DOB, no such a plateau was found, indicating the absence of chain entanglement. Another work on the rheology of the hyperbranched poly(ether ketone) (PEK) by Kwak [7] found that with increasing DOB, the dependence of the viscosity on the angular frequency decreases, implying a trend of approaching Newtonian fluid. The master curves of the HB PEK showed that the broadness of the rubbery plateau decreased with the increasing DOB, ultimately leading to complete absence of a rubbery plateau for DOB=0.67. All of these behaviors demonstrate that, with high generation number or DOB, hyperbranched polymers are less entangled and feature lower viscosity and flow activation energy.

In addition, to the low viscosity, the HBP also show other desirable properties such as good solubility and low crystallizability [8]. All of these properties will enhance the miscibility of HBP with other polymers, including the prepolymers of HPTs. Moreover, the miscibility of HBP could be tailored by end group adjustment and/or degree of branching without any modification of the polymer backbone, that latter of which usually involves sacrifice of chain rigidity and thus modulus and T_g . Several research groups [9–11] have shown that T_g and solubility of a HBP indeed depend dramatically on the end groups. For example, The T_g of a hyperbranched PEK [9] increased from 98 to 290 °C after it was end-capped by *p*-(carboxy)phenoxy groups. The phenol-terminated hyperbranched PEK was soluble in most of the organic solvent and aqueous K_2CO_3 or KOH solutions. After

being end-capped with fluorine groups, however, it became only moderately soluble in DMF.

An important application of HBPs is melt viscosity modifiers, a utility presumed in the literature (though without substantiation) to be attributed to their ‘molecular ball bearing’ nature. Several recent studies have revealed that the addition of a hyperbranched polymer could lower the viscosity of the polymer melts. Hsieh [12] studied the rheology the blends of Boltorn H[®] HBPs with different molecular weights. Before blending, the molecular weight Boltorn H[®] HBP showed shear thinning while the high molecular weight ones were Newtonian-like. After mixing the two HBPs with deferent molecular weight, the 1:1 blend became Newtonian-like and showed a lower viscosity than the both components at low frequency/shear rate (at higher frequency/shear rate, the low molecular weight component has lower viscosity because of the shear thinning). In other work by Kim [11], it was found that the blends of polystyrene with 5 wt% of their hyperbranched polyphenylene exhibited lower viscosity than the blends containing 0.1 wt% hyperbranched polymer despite the heterogeneity in the blends. Moreover, Huber [13] found that their hyperbranched poly(ether amide) can efficiently decrease the viscosity of polyamide 6 even at a low load of 0.1 wt%. In this case, the blend was noticed to be homogenous.

So far, there are several reports on the promising results about the toughening of epoxy resins [14–17] and BMI resins (Matrimid[®]) [18] with aliphatic hyperbranched polyesters. However, because the aliphatic polyester possesses low thermal stability and modulus, these systems showed significant compromise in either T_g or modulus. Recently, a plethora of heat-resistance HBPs, such as hyperbranched PEK [7,9,19–21], ether imide [10,22–27], aromatic polyester [4,28] and aromatic polyamide [8,29,30], have been reported. Despite this great variety, no study on the toughening of epoxy or BMI resin with any of these HBPs has been reported. In this paper, we present such an approach to toughening the bisphenol-A based bismaleimide (BPA-BMI) with one of our



Scheme 1. Chemical structures of Bisphenol-A BMI (BPA-BMI) and allyl-terminated hyperbranched polyimide (AT-PAEKI).

recently reported hyperbranched polyimides, AT-PAEKI (Scheme 1) [26].

2. Experimental

2.1. Materials

Scheme 1 shows the chemical structures of BPA-BMI (2,2-bis[4-(4-maleimidophenoxy)phenyl]propane) and AT-PAEKI. The preparation of AT-PAEKI was described in our previous paper [26] and the BPA-BMI was obtained via a custom synthesis by University of Dayton Research Institute. All the solvents and other chemicals involved were purchased from commercial sources and used as received.

A solvent casting method was used to prepare AT-PAEKI and BPA-BMI blends. First, AT-PAEKI and BPA-BMI were dissolved in a common organic solvent (THF). Then the solvent was evaporated at ambient conditions, followed by heating to 80 °C under vacuum. Transparent amber films were obtained by this method, indicating good miscibility between AT-PAEKI and BPA-BMI. Four blends containing 2, 4, 8 and 16 wt% AT-PAEKI were prepared and studied.

2.2. Crosslinking of BPA-BMI and blends

In a vacuum oven preheated to 130 °C, the uncured BPA-BMI and AT-PAEKI blends were degassed under vacuum in a silicone mold. Three hours later, the vacuum was released by purging with nitrogen and the prepolymer was allowed to cure isothermally at 130 °C for additional 12 h. After cooling back to room temperature, the partially cured samples were removed from the mold and moved to another oven preheated to 250 °C, and postcuring under this condition for 8 h. The resultant sample bars were dark amber but transparent, indicating a homogenous microstructure. We note that the degassing and curing conditions were optimized based on results of DSC and chemorheology experiments, which will be discussed in the following sections.

2.3. Thermal analysis

The differential scanning calorimetry (DSC) data of the blends were collected using a TA Instruments DSC2920. Thermogravimetric Analysis (TGA) was performed either on Perkin–Elmer TGA 7 thermogravimetric analyzer or on TA TGA 2950. A single ramping rate of 10 °C/min was applied for both DSC and TGA.

2.4. Chemorheology studies

Chemorheology studies on the prepolymer were performed using an ARES LS rheometer (TA Instruments, Inc.) equipped with parallel plates with a diameter of 25 mm operating in dynamic mode with a frequency of 10 rad/s. During the isothermal studies, the strain and the gap were automatically adjusted to maintain torque and axial (normal) force within the sensitive range of the transducer. In the case of non-isothermal

chemorheological experiment, a temperature ramping rate of 4 °C/min was employed. During the measurement, the strain was adjusted and the thermal expansion of the fixtures was automatically adjusted to maintain the same sample thickness through the temperature range. By this protocol, the viscosities of the prepolymer during the crosslinking were recorded.

2.5. Dynamic mechanical analysis (DMA)

The flexural moduli, loss tangent (damping), and heat distortion temperatures were measured with a TA Instruments DMA 2980 under nitrogen. A three-point bending fixture with a span of 20 mm was employed during the tests. All DMA samples were polished to 5 mm long, 2.5 mm wide and 1.5 mm thick with SiC sand paper (1200 grit). The amplitude of oscillation was set to 15 μm to ensure that the sample was in the linear region. The temperature ramping rate was 3 °C/min and the oscillation frequency was 1 s^{-1} . The heat distortion temperature, as defined herein, was assessed as the temperature at which the flexural modulus decreases by 25% from its room temperature value.

2.6. Hardness and modulus by nano-indentation

Nano-indentation experiments were performed to measure the hardness and Young's moduli of the samples. In these experiments, a MTS Nano Indentor by EG and G Instruments equipped with a typical pyramid-shaped tip was used. The depth of each indentation was 10,000 nm and the load vs. displacement curves were recorded during both the loading and unloading processes. Based on the unloading curve, the Young's moduli and hardness of the samples were calculated. Each sample was tested six times, each at different location, and the average were taken as shown with error bars illustrating the standard deviation. Before the test, the instrument was calibrated using a quartz standard.

2.7. Fracture toughness

Following ASTM D5045-99, the fracture toughness in terms of K_{IC} , the critical stress intensity factor, of neat BPA-BMI resin and its blend with 2, 8 and 16 wt% were measured. The single edge notched bending (SENB) geometry was adopted. To prepare the notched sample, the samples were molded and then polished to the size of length \times depth \times width (thickness) = 25 \times 5 \times 2.5 mm and a notch of 2 mm depth was made by a saw. Then a finer tip was generated by insertion of a fresh razor blade under a reciprocating (sawing) action. At last, a natural crack was initiated by lightly tapping a razor blade against the tip of the notch. The total length of the notch (45–55% sample width) was then measured using reflected light microscopy. Three point bending experiments on such specimens were performed at room temperature on an Instron 1011 equipped with a 50 N load cell. A displacement rate of 1 mm/min was employed and the flexural span was 20 mm. Load–displacement curves were recorded and the critical stress intensity factor, K_{IC} , calculated.

For the SENB geometry, the K_{IC} was calculated using the following equation

$$K_{IC} = YP_Q(B^{-1}W^{-1/2}) \quad (1)$$

Here Y is given by

$$Y = 6(a/W)^{1/2} \frac{\{1.99 - (a/W)[1 - (a/W)][2.15 - 3.93(a/W) + 2.7(a/W)^2]\}}{[1 + 2(a/W)][1 - (a/W)]^{3/2}} \quad (2)$$

Here B and W are the thickness and width of the sample; a is the total length of the notch plus the crack. The P_Q value here is equal to the maximum load since all the samples exhibited the brittle fracture behavior. Generally, a valid measurement must fulfill the following criteria, which ensures that the fracture follows the plain strain mechanism

$$B, a, (W - a) \geq 2.5 \left(\frac{K_Q}{\sigma_y} \right)^2 \quad (3)$$

where σ_y is the yield stress of the material for the temperature and loading rate of the test.

The validity of our measurement method was assessed by comparing our measured values against values for standard materials measured by us using the same method. In particular, we measured K_{IC} for diglycidyl ether of bisphenol-A (DER332[®]) cured with diaminodiphenylsulfone (DDS) and compared with the value reported in reference [31]. Our measurements gave $K_{IC} = 0.75 \text{ MPa m}^{1/2}$, which agreed well with the reference, $0.7 \text{ MPa m}^{1/2}$.

3. Results and discussion

3.1. Thermal analysis of BPA-BMI and its blends

AT-PAEKI has a significant effect on the cure of BPA-BMI. Fig. 1 shows the DSC thermograms of BPA-BMI, AT-PAEKI, and their blends with different compositions. The first exothermic peak at 270 °C in neat AT-PAEKI is ascribable to a Claisen rearrangement, involving the allyl ether terminal groups, while the second exotherm at 305 °C is due to a crosslinking reaction between the allylphenol groups. The BPA-BMI shows a sharp melting point at 83.5 °C and a crosslinking exotherm starting at 175 °C and reaching its maximum at 199 °C. In the blends, this curing peak shifts to higher temperature with increasing AT-PAEKI content. Specifically, with 1, 2, 5, 10 and 20 wt% AT-PAEKI, the exothermic peak temperature increases to 233.7, 235.1, 266.0, 273.2, and 275.1 °C, respectively. A bimodal curing peak is also evident in thermograms of all the blends, indicating more complex curing reaction than the neat BPA-BMI. Indeed, researchers have reported that, upon heating, AT-PAEKI can undergo a Claisen rearrangement, resulting in the formation of allylphenol groups. These allylphenol groups can then react with maleimide groups through a series of reactions such as ene-addition, Wagner-Jauregg, Diels-Alder, thermal rearrangement, and thermal crosslinking [32].

The DSC scan of the virgin BPA-BMI shows a T_m at 83.5 °C. After blending with AT-PAEKI, this melting transition disappears completely. Instead, a glass transition at about 56 °C becomes apparent in the DSC traces of all the blends. These observations of single T_g , disappearance of T_m , and the transparent appearance of the blends samples suggest homogeneity even before the crosslinking reaction. However, the glass transition temperature does not increase with the concentration of AT-PAEKI, which has a higher glass transition of 121.4 °C.

By thermogravimetric analysis (TGA), we found that the BPA-BMI blends were stable to 250 °C in air. As an example, the TGA results of the blend with 5 wt% AT-PAEKI are shown in Fig. 2. The sample was first ramped at 10 °C/min to a series of temperatures (220, 250, and 280 °C) and then annealed at that temperature to see if there was any persistent decomposition. Fig. 2 depicts such isothermal tests at 280 (top) and 250 °C (bottom). At 280 °C, the blend with 5 wt% AT-PAEKI undergoes a slow but steady weight loss. To the contrary, at 250 °C the weight loss stops after a few percent at an early stage, which is attribute to the removal of residual solvent or absorbed moisture.

Based on the TGA results, we used 250 °C as the final cure temperature. We note that this simple cure cycle—non-optimized—stands in contrast to a post-cure condition of 300 °C by Lincoln and co-workers applied to the Matrimid[™] 5292 two-component resin system [33]. This higher temperature post-cure led to a high final T_g of 350 °C. Fig. 3 shows the DSC of the blend with 5 wt% AT-PAEKI. The samples were first degassed at 130 °C and then cured at 250 °C for different lengths of time, such as 8, 12, 18 and 36 h. Then, the samples

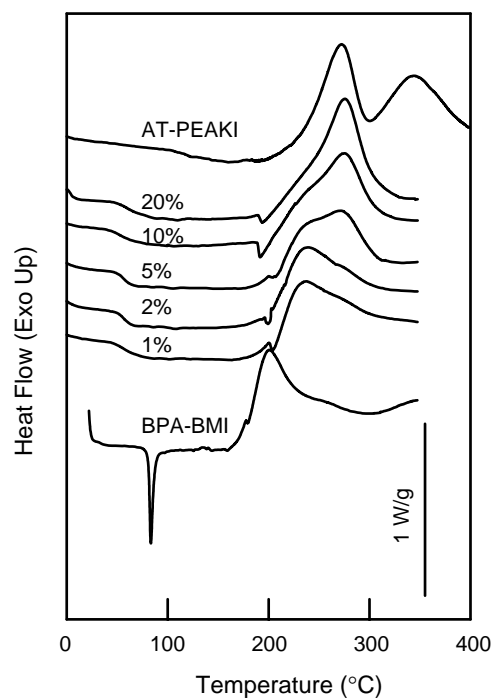


Fig. 1. The DSC traces of the neat BPA-BMI, AT-PAEKI and their blends with different compositions. The samples were cast from THF. The heating rate was 10 °C/min.

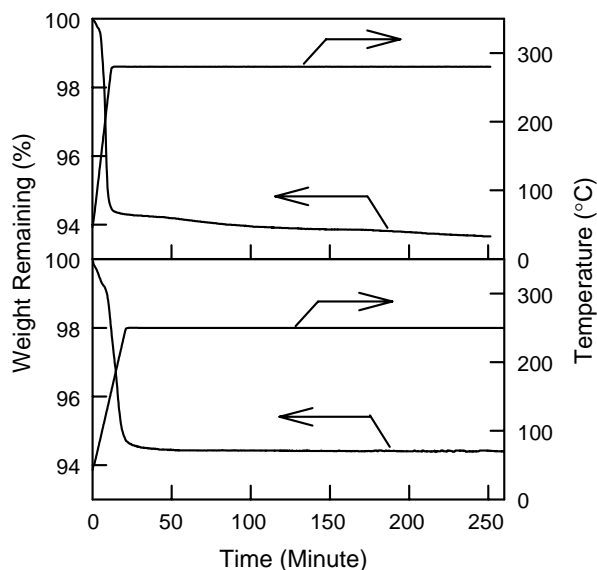


Fig. 2. Thermostability study of BPA-BMI blend with 5% AT-PAEKI by TGA. The top and bottom graphs indicate the weight loss of the blend BPA-BMI annealed in air at 250 and 280 °C, respectively. The sample was first ramped at 10 °C/min to the experimental temperature and subsequently annealed. An air environment was employed.

were ramped to 400 °C at 10 °C/min in the DSC and the heat flow traces recorded to detect any residual cure reactions. Exothermic peaks appear around 350 °C, which are attributed to residual cure. Moreover, the onset temperature and the peak area of the exothermic peak remains essentially the same for the four samples despite having been cured at 250 °C for different times. This indicates that the cure extent reaches a limiting value at 250 °C after 8 h. Based on these results, we employed 250 °C, 8 h as final curing step for our samples.

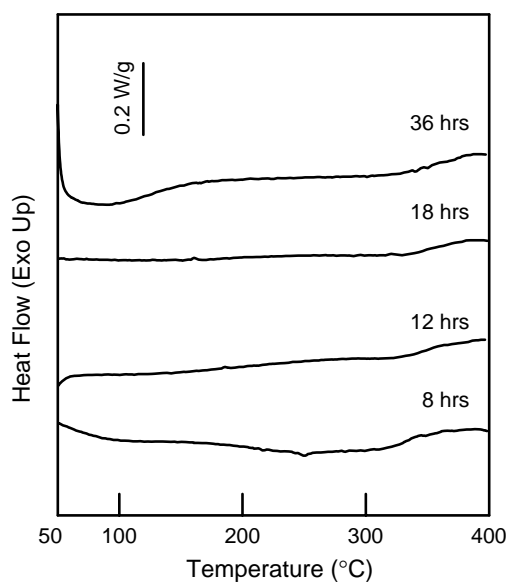


Fig. 3. The DSC traces of the isothermally cured BPA-BMI blends with 5 wt% AT-PAEKI. The samples were precured at 250 °C for 8, 12, 18 and 36 h before the DSC study.

The reason for incomplete cure, even at 250 °C, is the high T_g of the crosslinked resins. After cure, even just partially, the glass transition becomes higher than the curing temperature and the chain movement is constrained to a negligible level; i.e. vitrification occurs. As a result, the crosslinking groups cannot reach each other so that the cure reaction is halted. At higher temperatures, the chain movement is activated again and the cure reaction resumes, giving an exothermic peak in the DSC thermographs in Fig. 3.

3.2. Chemorheological characterization

Chemorheological characterization showed promising results that the addition of AT-PAEKI can facilitate processing by lowering viscosity. Empirically, prepreg processing and resin transfer molding (RTM) require the matrix resin to maintain a viscosity lower than 20 Pa s for a considerable period of time to ensure good flow and wetting. Fig. 4 shows results from isothermal chemorheology studies of BPA-BMI and its blend with 8 wt% AT-PAEKI. During this test, the samples were cured isothermally at four different temperatures (120, 130, 140, and 150 °C, as shown in the figure) in the rheometer and the increases in viscosity were recorded at these different temperatures. For BPA-BMI, the samples tested at higher temperatures had lower initial viscosities but underwent a more rapid viscosity increase, corresponding to the faster curing rates at higher temperature. At 130 °C, the sample maintains a low viscosity (less than 20 Pa s) for a substantial amount of time (2 h) and so we selected 130 °C to compare with AT-PAEKI modified samples.

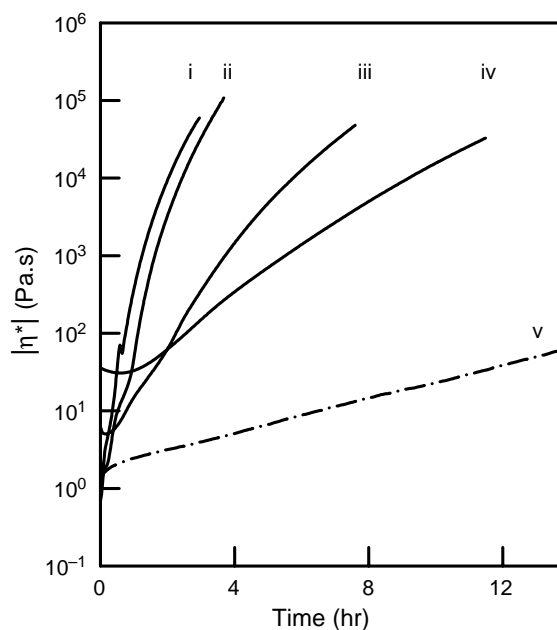


Fig. 4. The isothermal chemorheological study of neat BPA-BMI and its blend with 8 wt% AT-PAEKI at different temperatures: (i) BPA-BMI at 150 °C; (ii) BPA-BMI at 140 °C; (iii) BPA-BMI at 130 °C; (iv) BPA-BMI at 120 °C and (v) the 8 wt% blend at 130 °C. The frequency was 10 rad/s.

It is notable that the blend with 8 wt% AT-PAEKI featured a 4-fold decrease in initial viscosity and underwent slow and steady increase in viscosity with time at $T=130\text{ }^{\circ}\text{C}$. This shows that the presence of AT-PAEKI reduces viscosity substantially, while also modifying cure kinetics. As pointed out in the introduction section, this is likely due to a spherical conformation of the HBP additive that can mitigate entanglements of the host. Because of the ene-addition reactions between the allyl and maleimide groups, the cure reaction occurs at a higher temperature, which is manifested in Fig. 4 as a slower rate of viscosity increase. These results prove that the addition of AT-PAEKI, even in small amounts, can efficiently broaden the processing window of BPA-BMI.

Since the BPA-BMI maintains its viscosity at a value less than 20 Pa s for 2 h at $130\text{ }^{\circ}\text{C}$, we used that temperature for degassing and molding of our samples as described in Section 2. Indeed, we found that temperatures other than $130\text{ }^{\circ}\text{C}$, such as 120 and $140\text{ }^{\circ}\text{C}$, always gave bubbled samples for the neat BPA-BMI. Inspecting Fig. 4, one can see that at $120\text{ }^{\circ}\text{C}$, the viscosity $|\eta^*|$ is greater than 30 Pa s throughout, while at $T_{\text{cure}}=140\text{ }^{\circ}\text{C}$, the viscosity increases too fast (following a minimum) to allow complete bubble removal. Thus $130\text{ }^{\circ}\text{C}$ is an optimized pre-cure temperature.

AT-PAEKI can effectively broaden the processing window for the BMI resin, as revealed by non-isothermal chemorheology of neat BPA-BMI and its 4 wt% blend (Fig. 5). During this test, the sample temperature was ramped at $4\text{ }^{\circ}\text{C}/\text{min}$ and the viscosity recorded against temperature. At low temperature, the crosslinking of the samples is slow and can be neglected. In this case, the viscosity decreases with increasing temperature. As

the temperature increases, the cure reaction becomes dominating and the viscosity increases rapidly. Thus, a ‘U’ shaped curve is generated. In Fig. 5, the blend of BPA-BMI with 4 wt% AT-PAEKI has a lower viscosity than the neat BPA-BMI during the entire temperature range. From the curves for BPA-BMI (shown in duplicate), it is observed that the viscosity decreases until $150\text{ }^{\circ}\text{C}$, where the viscosity reached its minimum of 2 Pa s . Afterwards, the viscosity begins to increase. As the temperature reached $160\text{ }^{\circ}\text{C}$, the viscosity decreased slightly and then increased again. The experiment is quite repeatable; the second decrease in viscosity is an intrinsic feature of the sample and its cure reaction rather than some rheometric artifact.

We surmise that the cure of the BPA-BMI is a multi-step reaction. The first step happens around $150\text{ }^{\circ}\text{C}$ so that the viscosity increases at that temperature. At $160\text{ }^{\circ}\text{C}$, the first step of cure is almost completed and the second step barely starts. So the viscosity decreases again following a simple temperature effect. At temperatures higher than $170\text{ }^{\circ}\text{C}$, the second step commences and the viscosity increases again.

The curve of the 4 wt% blend features a low viscosity minimum ($\sim 0.1\text{ Pa s}$). At that viscosity, the torque is close to the lower limit of the rheometer’s transducer, as evidenced by a noisy baseline. Despite the noise, we can still estimate the temperature of the minimum viscosity to be about $180\text{ }^{\circ}\text{C}$, which is higher than that of the neat BPA-BMI. This observation agrees with the DSC result, which shows that the curing onset temperatures of the blends are higher than that of neat BPA-BMI. Beyond $190\text{ }^{\circ}\text{C}$, the viscosity undergoes a steady increase until $220\text{ }^{\circ}\text{C}$, where the increase slows down. As a reminder, the final cure step for sample bar preparation was a heat treatment at $250\text{ }^{\circ}\text{C}$ for 8 h.

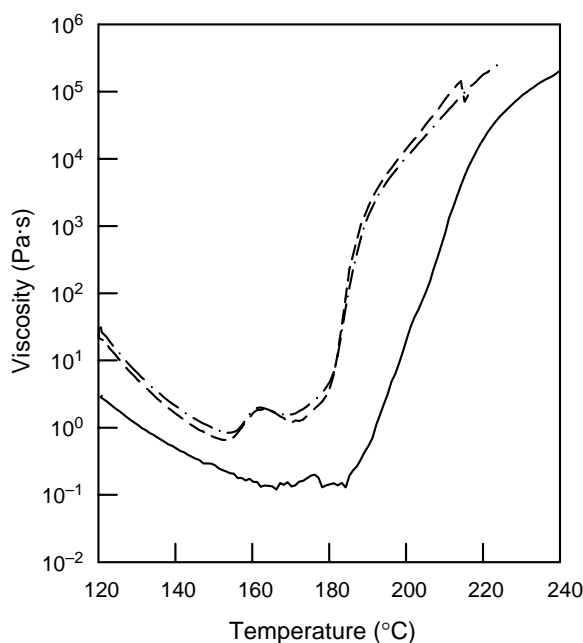


Fig. 5. The non-isothermal chemorheology study of the neat BPA-BMI (two dashed lines, duplicate) and blend with 4 wt% AT-PAEKI (solid line). The temperature ramping rate was $4\text{ }^{\circ}\text{C}/\text{min}$. An oscillation frequency of 10 rad/s was employed.

3.3. Mechanical properties

After crosslinking, AT-PAEKI can enhance the glass transition, modulus as well as the hardness of BPA-BMI as revealed by DMA and nano-indentation experiments. Fig. 6 presents the storage modulus (E') and $\tan \delta$ data of the crosslinked BPA-BMI resin and its blends with 2, 4, 8 and 16 wt% AT-PAEKI measured by DMA. At low temperature ($50\text{ }^{\circ}\text{C}$) the storage modulus (E') of cured BPA-BMI is 3.4 GPa while the blends with 2, 4, 8 and 16 wt% AT-PAEKI have an E' of 3.8, 3.6, 3.6 and 3.3 GPa , respectively. Clearly, E' increases with the content of AT-PAEKI at first and then decreases with increasing loading, giving a maximum modulus at 2 wt% of AT-PAEKI. We speculate that this trend is because of two distinct effects of AT-PAEKI, which are related to the backbone and the allyl terminal groups. Because the backbone of AT-PAEKI constitutes a high performance polyimide, it may act as hard filler and increase the modulus. In the other hand, the modulus may decrease as the crosslink density decreases by the allyl-maleimide ene reaction that may chain-extend without creating a network junction.

In the DMA traces, all samples except the one with 16 wt% AT-PAEKI undergo a storage modulus increase above the glass transition, indicating the existence of residual cure. As a

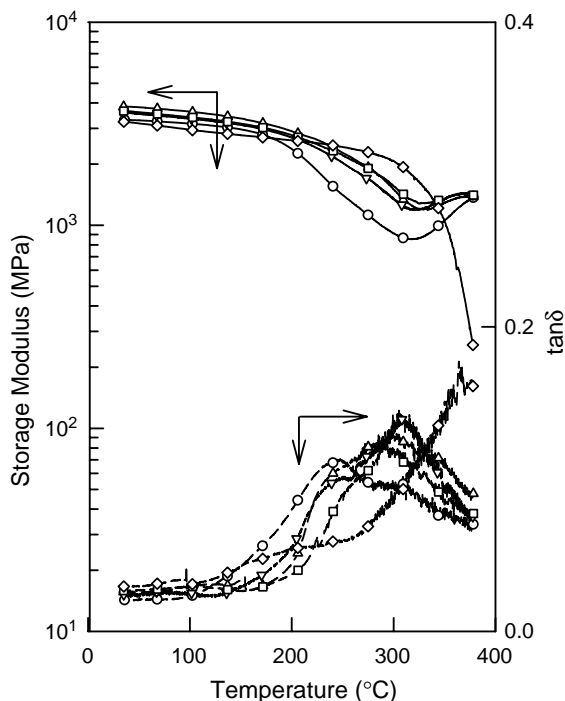


Fig. 6. The DMA study of neat BPA-BMI resin (○) and the blends with 2 (△), 4 (▽), 8 (□) and 16 (◇) wt% AT-PAEKI.

consequence of the residual cure, an extra peak in loss tangent appears above T_g , generating bimodal peaks (shoulder peaks in the case of the blends with 2 and 8% AT-PAEKI). From the first peak, the glass transition temperatures of the cured resins are identified. In particular, we determined from Fig. 6 that the T_g values of the neat and cured BPA-BMI and the blends with 2, 4 and 8 wt% AT-PAEKI were 244, 245, 249 and 264 °C, respectively. Clearly, the glass-transition temperature of the blends increased with the content of AT-PAEKI.

DMA of the blend with 16 wt% AT-PAEKI is quite different from the other samples. First, the observed glass transition is much higher than those of the other blends. In fact, the peak temperature of the loss tangent is higher than the upper limit of the DMA experiments temperature, which is 380 °C. As a result, the exact value was not determined and the residual cure of the sample is not observed in DMA. In order to compare the thermal-mechanical properties of the BPA-BMI and its blends, we used a modified heat distortion temperature (HDT). Here, HDT values were obtained from the modulus data by determining the temperature at which the storage modulus decreased by 25%. In Fig. 7, the HDT of the blends showed an accelerating increase with AT-PAEKI content. With 16 wt% AT-PAEKI, the HDT increased to about 251 °C from 194 °C, the HDT of neat BPA-BMI.

The 16 wt% blend undergoes a much more significant drop in storage modulus at the glass transition than the other blends, indicating a lower crosslink density (despite higher HDT). In particular, the storage modulus decreased to below 200 MPa for the case of 16 wt% blends, while the other blends and neat BPA-BMI maintain moduli higher than 1 GPa during the transition. We suggest that this observation results from higher

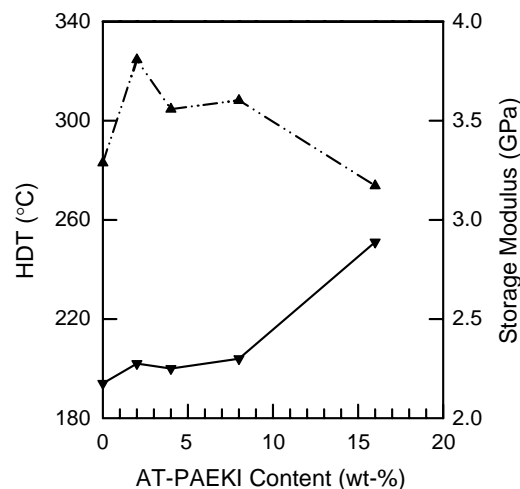


Fig. 7. The plot of the heat distortion temperature (HDT, ▼) and storage modulus (E' , ▲) at 50 °C against the content of AT-PAEKI. The heat distortion temperature was obtained from DMA storage modulus data (Fig. 6), as described in the text.

AT-PAEKI loading leading to more ene-addition reaction, lowering the crosslink density.

Indentation experiments were performed on the same samples to measure the hardness and Young's modulus and the results are shown in Fig. 8(a). Generally, a similar trend of modulus change as a function of AT-PAEKI content is observed by indentation as was revealed by DMA analysis (Fig. 7). That is, the 2 wt% blend has the highest Young's modulus, with this value decreasing with further increases in AT-PAEKI content. Theoretically, the Young's moduli measured by indentation should be slightly higher but very close to the storage moduli by DMA since the tangent delta values of these samples were very small. However, we observed that the Young's moduli from indentation are actually slightly lower than the storage moduli from DMA experiments.

Although the hardness data is more scattered (Fig. 8(b)), it is still clear that the hardness data followed same the trend as the modulus; i.e. the 2 wt% blend had the highest value and then the hardness decreased with AT-PAEKI content. The blends with 2, 4 and 8 wt% AT-PAEKI had statistically higher hardness than the neat BPA-BMI, while the blend with 16 wt% AT-PAEKI was very close to the neat BPA-BMI resin.

3.4. Fracture toughness

AT-PAEKI was found to be capable of toughening the BPA-BMI to some extent. We measured and compared the fracture toughness (in terms of K_{IC} , the critical stress intensity factor) of the neat BPA-BMI resin and the blend with 2, 8 and 16 wt% AT-PAEKI. For these measurements, a single edge notched bending (SENB) geometry was used by following the ASTM D5045-99 as described Section 2.

Fig. 9 presents the critical stress intensity factor values of the neat BPA-BMI and the blends. For each composition, multiple specimens were tested. The averages of K_{IC} as well as the error bars standing for the standard deviation are showed in

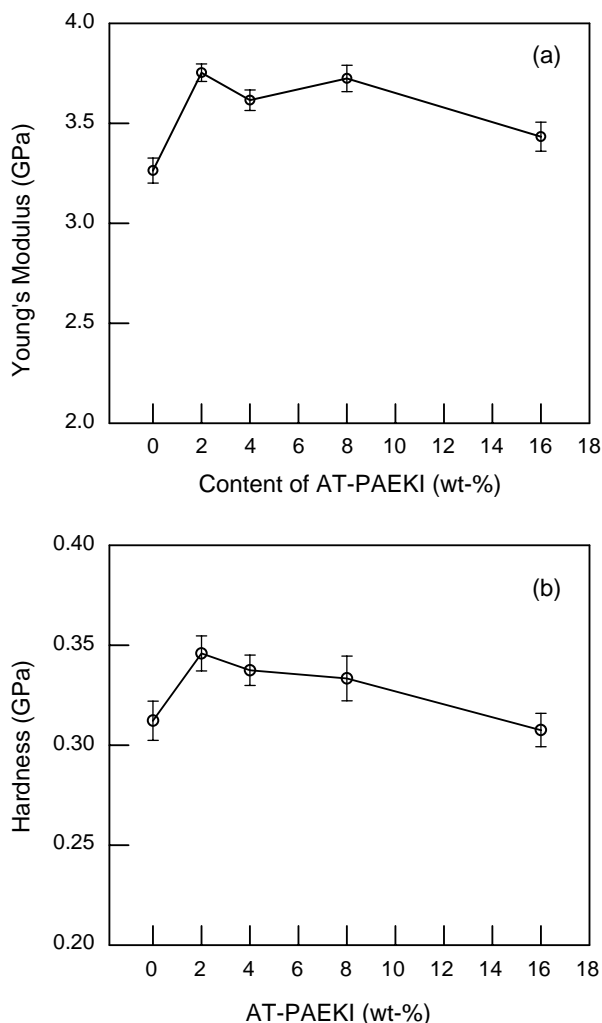


Fig. 8. The influence of the concentration of AT-PAEKI on the Young's modulus (a) and hardness (b) by nano-indentation. Each data point and its error bar stand for the average and standard deviation of six indentations at separated spots on the sample. All the blends showed higher moduli and hardness than the neat BPA-BMI sample.

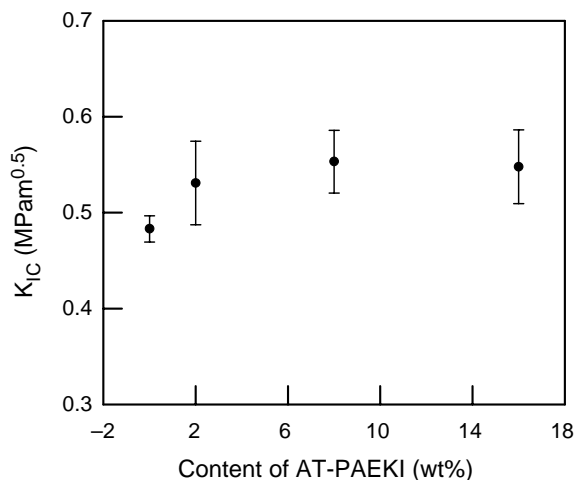


Fig. 9. The comparison of the fracture toughness, K_{IC} , of the neat BPA-BMI resin and the blend with 2, 8 and 16 wt% AT-PAEKI, measured following ASTM D5045-99.

the figure. The average fracture toughness of BPA-BMI values 0.48 MPa $m^{1/2}$, while all the blends showed slightly higher K_{IC} values (0.53, 0.55 and 0.55 MPa $m^{1/2}$). Statistically, the difference in K_{IC} between neat BPA-BMI and 8 and 16 wt% blends is significant but small.

In this BPA-BMI/AT-PAEKI system, only modest toughening effect was observed. We attribute this to homogeneity and the relatively low content of the allyl groups. Generally speaking, an immiscible system will help in the toughening of the matrix resin because the cavitations of the dispersed phase could absorb more energy and thus stabilize the crack. In our case, this toughening mechanism is not available since our blends are homogeneous. The possible toughening mechanism here is by lowering the crosslinking density via the ene addition reactions, which was used in the commercial product, Matrimid® 5292. In Matrimid® system, the molar ratio of the allyl group over the maleimide group is 1. However, this ratio is much lower in our system.

Thus, we may consider two approaches to increase the toughness more. The first one would be to increase the content of AT-PAEKI. However, this approach is not so practical given the relative complexity (and thus cost) of AT-PAEKI synthesis. The second approach would be to tune the miscibility of AT-PAEKI with BPA-BMI so that we can introduce some heterogeneity through limited phase separation. As discussed in the introduction section, the miscibility can be tailored by varying the degree of branching without any sacrifice in the rigidity of the polymer backbone. Alternatively, multiple endcappers can be employed to tune miscibility. All of these make the second approach more feasible and represents an area of planned research.

4. Conclusions

In this study, the toughening of the bisphenol-A bismaleimide with a newly synthesized hyperbranched polyimide, AT-PAEKI, is reported. Unlike conventional toughening additives, AT-PAEKI was found to be capable of reducing the processing viscosity, widening the processing window, increasing the glass transition temperature, modulus, hardness and toughness. We believe that these properties are directly related to the macromolecular architecture of AT-PAEKI, which is a hyperbranched (allowing viscosity reduction), high performance (increase T_g and modulus) and allyl group terminated (increasing the fracture toughness) polyimide. These features encourage the use of such high performance hyperbranched polymers as a new class of tougheners for HPTs. Because of the homogeneity and low concentrations of AT-PAEKI, only a modest toughening effect was observed. To increase the toughness, we suggest introducing limited heterogeneity by altering the degree of branching or using multiple end-cappers, in addition to the allyl group.

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